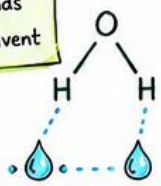
WATER CHEMISTRY

H_2O → Polar Molecule
Forms H-bonds
Universal solvent



IN ONE LINE

Study of chemical properties & behaviour of water → Important for life & environment.

WATER IN NATURE

- Present in oceans, rivers, ponds, lakes, glaciers etc.
- Rainwater → pure (no salts) contains dissolved gases
- Soft water → forms lather with soap → good for laundry & cleaning

① EFFECT OF IMPURITIES

A. PHYSICAL IMPURITIES

ⓘ Colour
→ Due to Fe, Mn, Cr, Co salts, algae, weed etc.
Hexavalent Cr → Toxic

ⓘⓘ Turbidity
→ Fine suspension of clay, silt etc.

ⓘⓘⓘ Taste
→ $NaHCO_3^-$ → soapy taste
$Al_2(SO_4)_3$, $FeSO_4$, $MnSO_4$ → bitter taste

ⓘⓥ Odour
→ Organic compounds of N, S, P & organics like phenols, esters etc.

B. CHEMICAL IMPURITIES

ⓘ Inorganic & organic chemicals from dyes, drugs, paints, insecticides, pesticides etc.

ⓘⓘ Acidity due to dissolved NO_2, SO_2
→ forms H_2CO_3, H_2SO_4 etc.

C. BIOLOGICAL IMPURITIES

Fungi, viruses, bacteria, parasites worms etc.

② ACIDITY OF WATER

- Due to mineral acids, free CO_2, Fe/Al sulfates, Mg chlorides etc.
- pH < 7
- Acidic water + iron → corrosion in pipes & boilers

IMPORTANCE

Determination of acidity is very important. ☆

③ ALKALINITY OF WATER

- Due to presence of:
  1. Caustic alkalinity → OH^-, CO_3^{2-}
  2. Bicarbonate alkalinity → HCO_3^-
- Ions from Ca, Mg, Na, K salts etc.
- Some salts → hardness (not alkalinity)

④ HARDNESS OF WATER

- Prevents soap from lathering easily.
- Due to soluble bicarbonates, chlorides & sulfates of Ca & Mg.
- Ca^{2+} & Mg^{2+} ions react with soap → white ppt (soap scum) → no lather.
- Main component → Calcium stearate (from sodium stearate in soap)

Hard water + Soap → White ppt (Soap scum) → Poor lather ✗

REACTION

$$2C_{17}H_{35}COO^-_{(aq)} + Ca^{2+}_{(aq)} \longrightarrow (C_{17}H_{35}COO)_2Ca_{(s)}$$

⑤ TYPES OF HARDNESS

1. TEMPORARY HARDNESS

- Due to $Ca(HCO_3)_2$, $Mg(HCO_3)_2$
- Dissolve → Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}
- Removed by:
  - ✓ Boiling
  - ✓ Lime treatment [$Ca(OH)_2$]

ON BOILING

Bicarbonate → Carbonate → $CaCO_3$ ppt ↓ → Softer water

2. PERMANENT HARDNESS

- Due to soluble salts of Ca & Mg in form of:
  - Chlorides
  - Sulfates
  - Phosphates
  - Nitrates
  - etc.
- Not removed by boiling
- Removed by:
  - ✓ Water softener
  - ✓ Ion-exchange column

Ion Exchange Column

QUICK COMPARISON

Temp.	Perm.
Bicarbonates	Chlorides
$Ca(HCO_3)_2$	Sulfates
$Mg(HCO_3)_2$	Phosphates
Boiling ✓	Boiling ✗
Lime treat.	Softener/ Ion-exchg.

⑥ DEGREE OF HARDNESS

- Measures conc. of dissolved Ca^{2+} & Mg^{2+} in water.
- Expressed as $CaCO_3$ equivalent for easy comparison.

WHY $CaCO_3$?

- ✓ Molecular weight = 100
- ✓ Equivalent weight = 50
- ✓ Easy calculations
- ✓ Insoluble in water → forms ppt

1 mole $CaCO_3$ reacts with same amount of soap as 1 mole $CaCl_2$, $MgSO_4$ & other divalent salts.

FORMULA

$$\text{Degree of hardness} = \frac{\text{Weight of salt causing hardness} \times \text{Molecular weight of } CaCO_3}{\text{Molecular weight of salt causing hardness}}$$

$CaCO_3$ MW = 100

⑦ UNITS OF HARDNESS

Unit	Meaning
1. ppm	Parts of $CaCO_3$ equivalent hardness per 10^6 parts of water
2. mg/L	Milligrams of $CaCO_3$ equivalent hardness per litre of water
3. °Cl (Clark's degree)	Parts of $CaCO_3$ equivalent hardness per 70,000 parts of water
4. °Fr (French degree)	Parts of $CaCO_3$ equivalent hardness per 10^5 parts of water
5. meq/L	Milliequivalents of $CaCO_3$ equivalent hardness per litre of water

IMPORTANT NOTE

1 ppm = 1 mg/L

☆ KEY TAKEAWAYS

- Impurities → Physical, Chemical, Biological
- Acidity → pH < 7 → Corrosion
- Alkalinity → OH^-, CO_3^{2-}, HCO_3^-
- Hardness → Ca^{2+}, Mg^{2+} → No lather
- Temporary → Bicarbonates → Boiling ✓
- Permanent → Chlorides/Sulfates etc. → Boiling ✗
- Standard for hardness → $CaCO_3$ (MW = 100)
- Units → ppm, mg/L, °Cl, °Fr, meq/L

8 PRACTICE QUESTIONS

1. What causes temporary hardness?
2. Which ions mainly cause hardness?
3. Is permanent hardness removed by boiling?
4. Why is $CaCO_3$ used as the standard for hardness?
5. What is the pH of acidic water?
6. Name the two types of alkalinity.

ANSWERS KEY

1. Ca/Mg bicarbonates → $Ca(HCO_3)_2$, $Mg(HCO_3)_2$
2. Ca^{2+} and Mg^{2+}
3. No ✗
4. MW = 100, Eq. wt. = 50, easy calculations, insoluble.
5. pH < 7
6. Caustic alkalinity & Bicarbonate alkalinity.

⚠ **PRO TIP: 3 KEY TERMS → Don't confuse!**

Acidity (pH<7) → Corrosion
Alkalinity (OH^-/CO_3^{2-}/HCO_3^-)
Hardness (Ca^{2+}/Mg^{2+}) → No lather, scale

1 RELATIONSHIP BETWEEN HARDNESS UNITS ☆

IMPORTANT CONVERSIONS

1 ppm = 1 mg/L = 0.07 °Cl = 0.1 °Fr = 0.02 meq/L

1 °Cl = 1.43 °Fr = 14.3 ppm = 14.3 mg/L

CLASSIFICATION OF WATER

TYPE OF WATER	HARDNESS (mg/L as $CaCO_3$)
Soft	Below 75
Moderately hard	76 – 150
Hard	151 – 300
Very hard	Above 300

2 NUMERICAL PROBLEMS

1 Calculate:
- Temporary hardness
- Permanent Mg hardness
- Total permanent hardness
- Total hardness

Given (per litre):
- $Ca(HCO_3)_2$ = 12.2 mg
- $Mg(HCO_3)_2$ = 8.2 mg
- $MgSO_4$ = 5.6 mg
- $MgCl_2$ = 6.2 mg
- $CaSO_4$ = 10.3 mg

2 Water contains 200 mg/L $CaSO_4$.
Calculate hardness in:
- mg/L as $CaCO_3$
- ppm
- °Cl
- °Fr

3 How many grams of $MgCl_2$ produce hardness of 76 ppm ?

Given:
Molecular weight of $MgCl_2$ = 95 g

4 500 mL water has hardness equivalent to 50 mL of 0.1 N $CaSO_4$.
Find hardness in ppm.

Given:
Molecular weight of $CaSO_4$ = 136 g

5 Water contains:
- $Ca(HCO_3)_2$ = 16.2 mg/L
- $CaSO_4$ = 6.8 mg/L
- $MgSO_4$ = 3.6 mg/L

Calculate:
- Permanent hardness
- Temporary hardness
- In °Cl

3 PROBLEMS ASSOCIATED WITH HARD WATER ☆

A. DOMESTIC PROBLEMS

1 Poor lathering
- Hard water → soap does not lather easily
- More soap required
- Soap wastage

2 Scum formation
Ca/Mg + soap → insoluble salts
→ Scum sticks to clothes & utensils.

3 Scaling
$CaCO_3$ + $MgCO_3$ deposits → layer formation
Found in:
- Kettles
- Boilers
- Washing machines
- Heaters

→ Efficiency decreases.

4 Clothes
Salt deposition → clothes become:
- Stiff
- Dull

B. INDUSTRIAL PROBLEMS

1 Boiler & pipe scaling
- Hard water → thick, adherent scales
- Poor heat transfer
- Overheating
- Boiler bursting
- Pipe blockage

2 Increased fuel consumption
Poor heat transfer → more heating required → More fuel consumed

3 Industrial damage
Water quality is important in:
- Textile industry
- Paper industry
- Dyeing industry

C. HEALTH-RELATED PROBLEMS

1 Temporary hardness
→ May cause digestive issues.

2 Excessive hardness
→ May contribute to kidney stone formation in sensitive individuals.

4 BOILER PROBLEMS

WHAT IS A BOILER?

Boiler converts water → steam using heat energy.

Heat source:
- Coal
- Oil
- Gas
- Biomass
- Electricity

MAIN USES

★ Power generation
Steam → turbines → electricity

★ Industrial heating
Textile, sugar, paper, chemical, food industries

★ Mechanical work
Steam engines, pumps, compressors

★ Sterilization & cleaning
Food, pharmaceutical & hospital industries

MAJOR BOILER PROBLEMS

Water impurities can cause:
1. Sludge & Scale Formation
2. Boiler Corrosion
3. Caustic Embrittlement

5 SLUDGE & SCALE FORMATION

Hard water in boiler:
Ca^{2+} / Mg^{2+} salts → deposits inside boiler
These deposits are mainly:
→ Scale
→ Sludge

CAUSES OF SCALE

1 Calcium bicarbonate
On heating:
$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2$
$CaCO_3$ insoluble → precipitates
→ scale

2 Magnesium salts
Hydrolysis:
$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl$
$Mg(OH)_2$ → insoluble precipitate
→ deposit

3 Calcium sulfate
$CaSO_4$ → solubility ↓ as temperature ↑
→ Precipitation → scale

4 Silicates & Phosphates
Ca/Mg silicates & phosphates
→ Sparingly soluble in cold water
→ Completely insoluble in hot water
→ Stick to boiler walls → hard coatings

A. SCALE

Definition: Scale = hard, adherent, crystalline deposits firmly attached to boiler surfaces.

6 SLUDGE

Definition: Sludge = loose, soft, non-adherent deposits.

Unlike scale → Sludge easily washed / blown out.

Usually settles at bottom of the boiler.

DISADVANTAGES OF SLUDGE

1 Fuel wastage
- Sludge → poor heat conductor
→ More heating required
→ More fuel used

2 Decreased efficiency
- Poor heat conduction
→ Boiler efficiency ↓

3 Pipeline choking
- Sludge settles in pipe connections
→ Water circulation ↓
→ Pipelines may choke

QUICK DIFFERENCE

FEATURE	SCALE	SLUDGE
Nature	Hard	Soft
Type	Adherent	Non-adherent
Structure	Crystalline	Loose
Attachment	Firmly sticks to walls	Usually settles at bottom
Removal	Difficult to remove	Easily washed / blown out

IN ONE LINE

Hard water → deposits in boiler → sludge / scale → poor heat transfer → efficiency ↓ + fuel consumption ↑

EXAM TIP

Remember the sequence:
Hard water → Scale/Sludge → Heat transfer ↓ → Fuel consumption ↑ → Boiler efficiency ↓

① DISADVANTAGES OF SCALE & IN BOILER

① Wastage of Fuel
- Scale → low thermal conductivity
- More heat required
- Boiler heated to higher temp.
- Fuel consumption ↑

② Bagging
- Scale causes overheating
- Boiler material → softer, weaker, distorted
- Boiler unsafe for steam pressure

③ Decrease in Efficiency
- Scale deposits on valves, condensers
- Partially choke components
- Proper operation affected
- Boiler efficiency ↓

④ Danger of Explosion
- Uneven expansion → cracking of scale
- Water touches hot metal
- Sudden steam formation
- Sudden pressure ↑
- Boiler explosion

② PREVENTION OF SLUDGE & SCALE FORMATION

A. Cleaning Operations (for sludge)
- Concentrated boiler water is partly removed
- Fresh water added
- Concentration of deposits ↓

B. External Treatment (before boiler)
Water is treated before entering boiler.

Important methods:
1. Lime-Soda Process
2. Zeolite Process
3. Ion-Exchange Process

C. Internal Treatment (inside boiler)
Called **SEQUESTRATION**

Definition: Preventing an ion from exhibiting its usual properties.

Done by:
- Converting ion into another form
  OR
- Forming a complex with another compound

③ INTERNAL BOILER CONDITIONING

Four main methods used inside the boiler.

① Colloidal Conditioning
Colloidal organic substances added to boiler water.

Examples: Kerosene, Glue, Tannin

→ Coat scale-forming precipitates
→ Prevent coagulation
→ Salts remain as sludge
→ Removed by blowdown operation

Flow: Scale-forming salts → Colloidal substance → coating → no coagulation → sludge → blowdown

② Phosphate Conditioning
Hard scale-forming salts converted into soft phosphate salts.
Removed by blowdown.

Reaction:

$$3CaCl_2 + 2Na_2PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$

Common phosphates:
- NaH_2PO_4
- Na_2HPO_4
- Na_3PO_4

③ Carbonate Conditioning
Prevents deposition of sulfate salts.
Na_2CO_3 added to boiler water.
$CaSO_4 \rightarrow CaCO_3$ (loose sludge)
Removed by blowdown.

Reaction:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

④ Calgon Conditioning
Calgon = Sodium hexametaphosphate
Added to boiler water.
Forms soluble complex with scale-forming salts.

Reaction:

$$2CaSO_4 + Na[Na_4P_6O_{18}] \rightarrow [Ca_2P_6O_{18}]^{2-} + 2NaSO_4$$

④ BOILER CORROSION

Definition:
Destruction of boiler metal due to chemical or electrochemical reactions.

May involve: water, dissolved oxygen, acids, salts.

Effects:
- Corrosion → metal strength ↓
- May cause → Leakage
  Pitting
  Boiler failure

⑤ CAUSES OF BOILER CORROSION (Four Major Causes)
1. Dissolved Oxygen
2. Carbon Dioxide
3. Acidic Impurities
4. Galvanic Corrosion

① PRESENCE OF DISSOLVED OXYGEN
- Water contains dissolved O_2
- On heating → O_2 released
- O_2 reacts with iron → rust formation

Reaction:

$$4Fe + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 \rightarrow Fe_2O_3 \cdot xH_2O \text{ (Rust)}$$

Removal: Add chemicals such as Na_2SO_3, Na_2S, N_2H_4

⑥ CORROSION DUE TO CARBON DIOXIDE
- CO_2 may be dissolved in water or produced from decomposition of bicarbonate salts at high boiler temperature.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$
$$\downarrow$$
$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$\downarrow$$

Carbonic acid makes water acidic
→ Acid attacks boiler metal
→ Corrosion

Removal: Add calculated amount of Ammonium hydroxide (NH_4OH)

⑦ CORROSION DUE TO ACIDIC IMPURITIES
- Some salts undergo hydrolysis to produce acids.

Example:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

HCl is strongly corrosive
→ Metal attacked
→ Boiler corrosion

⑧ GALVANIC CORROSION
- Occurs when two dissimilar metals come into contact in boiler water.
- One metal acts as Anode
- Other acts as Cathode
- Anodic metal corrodes faster

⑨ TYPES OF BOILER CORROSION

Two main types:
1. Pitting Corrosion
2. Uniform Corrosion

① PITTING CORROSION
Definition: Localized form of corrosion.
Small pits or holes form on metal surface.
- Penetrate deeply
- Affect localized areas
- Rest surface appears unaffected

Causes:

A. Dissolved Oxygen
- O_2 attacks particular spots
- Tiny regions form → pits grow

Reaction:

$$4Fe + O_2 + 2H_2O \rightarrow 4Fe(OH)_2$$

B. Chloride Ions
- From $MgCl_2$, NaCl etc.
- Cl^- breaks protective oxide layer of iron
- $MgCl_2$ hydrolysis → HCl
- HCl attacks metal → pits form

C. Scale & Sludge Deposits
- Deposits on boiler surfaces create differential aeration cells
- Areas below deposit become anodic
- Corrosion occurs at these regions

Effects: • Pipe leakage • Boiler failure • Sudden failure • Explosion

② UNIFORM CORROSION
Definition: General thinning of boiler metal surface.
- Thinning occurs evenly over the exposed area.

Difference:

	Uniform Corrosion	Pitting Corrosion
Nature	Even / widespread	Localized / deep holes
Metal loss	Even thinning	Localised attack
Appearance	Uniform surface	Small pits / holes

⑩ CAUSTIC EMBRITTLEMENT

Definition:
Caustic embrittlement is a type of corrosion caused by highly alkaline boiler water.
Accumulation of caustic substances causes boiler material to become **BRITTLE.**

IN ONE LINE
Boiler impurities → sludge / scale → poor heat transfer & overheating; O_2, CO_2, acids, salts → corrosion; high alkalinity → caustic embrittlement.

EXAM TIP
Remember the chain:

Hard Water Impurities → Scale / Sludge Formation → Heat Transfer ↓ Overheating → Boiler Problems (Corrosion / Explosion)

QUICK RECALL TABLE

Scale	Hard, adherent deposit
Sludge	Loose, non-adherent deposit
Internal treatment	Sequestration (prevent ions from acting)
O_2 in water	Causes rust formation
CO_2 in water	Forms H_2CO_3 (acid) → corrosion
Acidic salts	Hydrolysis → acids (e.g., HCl) → corrosion
Galvanic corrosion	Dissimilar metals → one corrodes

① CAUSTIC EMBRITTLEMENT – MECHANISM

- In lime-soda softening, slight excess of Na_2CO_3
- In high pressure boilers:

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

Excess Na_2CO_3 → hydrolysis → NaOH

NaOH → makes water highly alkaline

NaOH enters minute hairline cracks, bends, joints, riveted / stressed parts

Concentrated NaOH attacks metal

Iron dissolves as sodium ferrate (Na_2FeO_2)

Boiler material becomes BRITTLE

Dangerous at bends, joints, rivets

↓

Boiler failure may occur!

② PREVENTION OF CAUSTIC EMBRITTLEMENT

① Use Sodium Phosphate

- Use sodium phosphate instead of sodium carbonate as softening agent → reduces formation of excessive NaOH.

② Add Tannin or Lignin

- Tannin / lignin added to boiler water → blocks hairline cracks → prevents infiltration of NaOH.

③ Add Na_2SO_4

- Na_2SO_4 can block hairline cracks → prevents NaOH from entering cracked regions.

Note: Na_2SO_4 can form $CaSO_4$ scale. Therefore, Na_3PO_4 is preferred.

③ WATER SOFTENING TECHNIQUES

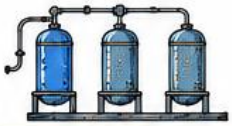
Industrial water must be sufficiently pure. Hardness causing salts must be removed before use.

Definition:

Softening of water = process of removing hardness causing salts from water.

Three main industrial methods:

1. Lime-Soda Process
2. Base-Exchange / Zeolite Process
3. Demineralization / Ion-Exchange Process



④ LIME-SODA PROCESS

Definition: In lime-soda process, soluble hardness causing substances are converted into insoluble precipitates.

Chemicals used:

- Lime → $Ca(OH)_2$
- Soda → Na_2CO_3

Precipitates formed are removed by → Settling + Filtration

⑤ REACTIONS WITH LIME ($Ca(OH)_2$)

A. Removal of Temporary Hardness

- Calcium bicarbonate:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

Insoluble ppt.

- Magnesium bicarbonate:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3\downarrow + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow$$

⑥ REMOVAL OF PERMANENT Mg HARDNESS

- Magnesium chloride:

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$$

- Magnesium sulfate:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4$$

Mg^{2+} ion is removed as insoluble $Mg(OH)_2\downarrow$

⑦ REMOVAL OF DISSOLVED IRON & ALUMINIUM SALTS

- Ferrous sulfate:

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$$

$$Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3\downarrow$$

- Aluminium sulfate:

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4$$

Fe and Al removed as insoluble hydroxide precipitates.

⑧ REMOVAL OF DISSOLVED CO_2 & H_2S

- Carbon dioxide:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$$

- Hydrogen sulfide:

$$H_2S + Ca(OH)_2 \rightarrow CaS\downarrow + 2H_2O$$

⑨ REMOVAL OF FREE MINERAL ACIDS

- Hydrochloric acid:

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$$

- Sulfuric acid:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

⑩ REACTIONS WITH SODA (Na_2CO_3)

$CaCl_2$ and $CaSO_4$ cause permanent Ca hardness. They also produced when lime reacts with mineral acids. These salts react with soda.

- Calcium chloride:

$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3\downarrow$$

- Calcium sulfate:

$$CaSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CaCO_3\downarrow$$

Ca^{2+} → $CaCO_3$ precipitate → Permanent Ca hardness removed.

⑪ ROLE OF COAGULANTS

- Precipitates formed are very fine.
- Some remain suspended even after filtration.
- Coagulants are added.

Examples: Sodium aluminate, Aluminium sulfate

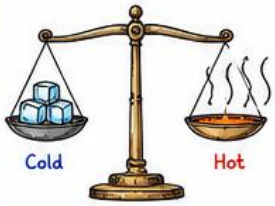
- These coagulants → trap fine precipitates → make them heavier → help them settle down.

⑫ TYPES OF LIME-SODA PROCESS

Two types:

① Cold Lime-Soda Process

② Hot Lime-Soda Process



⑬ COLD LIME-SODA PROCESS

- Lime & soda mixed with water at room temperature.
- At room temp., precipitates are very fine, do not settle easily, may pass through filter.
- Therefore, coagulants are required.

Coagulants: Alum, $Al_2(SO_4)_3$, $NaAlO_2$

- Undergo hydrolysis → gelatinous $Al(OH)_3$ → traps fine precipitates.

Special advantage of $NaAlO_2$:

- Helps remove Silica
- Removes Oil, if present in water.

Residual hardness: 50–60 ppm

⑭ HOT LIME-SODA PROCESS

Water treated with lime & soda at 80–150°C

① Faster reaction (Temp. ↑ → rate ↑)

② Greater softening capacity

③ Better sludge settling → No coagulant required

④ Dissolved gases removed almost completely

⑤ Easier filtration (Viscosity ↓)

⑥ Lower residual hardness

Residual hardness: 20–30 ppm

⑮ COLD vs HOT LIME-SODA PROCESS

Feature	Cold Process	Hot Process
Temperature	Room temperature	80–150°C
Reaction rate	Slower	Faster
Coagulant	Required	Not required
Lime consumption	More	Less
Residual hardness	50–60 ppm	20–30 ppm

⑯ ADVANTAGES OF LIME-SODA PROCESS

① Economical
- The process is economical.

② Reduced Corrosion
- Treatment produces pH > 7 → Corrosion decreases.
- Helps kill pathogenic bacteria to a large extent.

③ Reduced Mineral Content
- Quantity of minerals is reduced.

IN ONE LINE

Lime-soda process converts soluble hardness salts → insoluble precipitates → removed by settling & filtration.

EXAM TIP

Cold process → RT, coagulant required, ↑ 50–60 ppm

Hot process → 80–150°C, no coagulant, 20–30 ppm

KEY SEQUENCE

① Hard water
② Add lime & soda
③ Form insoluble ppt.
④ Coagulant (cold)
⑤ Settling
⑥ Filtration
⑦ Soft water

① DISADVANTAGES OF LIME-SODA PROCESS

① Large Sludge Production
- Large quantity of sludge is produced.
  → Creates sludge disposal problems.

② Careful Operation Required
- The process requires careful operation.

③ Residual Hardness
- Residual hardness is not sufficiently low for boiler use.

② ZEOLITE PROCESS

Zeolites are also known as Permutit.

They are hydrated crystalline sodium aluminosilicates.

$$Na_2O \cdot Al_2O_3 \cdot x SiO_2 \cdot y H_2O$$

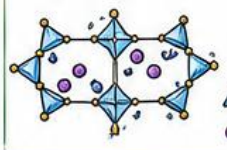
where,

$x = 2 - 10$

$y = 2 - 6$

③ STRUCTURE OF ZEOLITE

- Zeolite crystal is formed by linking SiO_4 tetrahedra.
- Some $Si^{2+} \rightarrow Al^{2+}$
- Extra positive charge needed for electrical neutrality.
- Therefore, Na^+ or K^+ ions are incorporated.
- Linking of tetrahedra produces an open structure with cavities.
- Inside cavities → Na^+/K^+ ions are loosely held.



④ ION-EXCHANGE PROPERTY OF ZEOLITE

Zeolite can exchange:
Monovalent cations → Divalent cations

Na^+ in zeolite ↓ exchange with Ca^{2+} / Mg^{2+} in hard water

Therefore, zeolites are used as water softeners.

Applications:
- Domestic water softening
- Industrial water softening

⑤ TYPES OF ZEOLITES

There are two types:

① Natural Zeolites
- Examples:
  Thomsonite : $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$
  Natrolite : $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$
- Generally non-porous
- Less efficient as water softeners

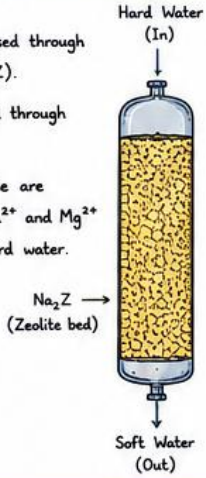
② Synthetic Zeolites
- Prepared by heating solutions of sodium silicate, aluminium sulfate, sodium aluminate.
- White coloured, called Permutit.
- Porous, gel-like structure.
- Much higher exchange capacity than natural zeolites.

⑥ SOFTENING BY ZEOLITE PROCESS

Hard water is passed through zeolite bed (Na_2Z).

Water is percolated through the bed.

Na^+ ions of zeolite are exchanged with Ca^{2+} and Mg^{2+} ions present in hard water.



Important Reactions

- Calcium bicarbonate
  $Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$
- Magnesium bicarbonate
  $Mg(HCO_3)_2 + Na_2Z \longrightarrow MgZ + 2NaHCO_3$
- Calcium chloride
  $CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$
- Calcium sulfate
  $CaSO_4 + Na_2Z \longrightarrow CaZ + Na_2SO_4$
- Magnesium chloride
  $MgCl_2 + Na_2Z \longrightarrow MgZ + 2NaCl$
- Magnesium sulfate
  $MgSO_4 + Na_2Z \longrightarrow MgZ + Na_2SO_4$

Key Idea
Ca^{2+} / Mg^{2+} → captured by zeolite
Na^+ → released into water

⑦ REGENERATION OF ZEOLITE

- During operation, Na^+ in zeolite gets exchanged with Ca^{2+} / Mg^{2+}.
- After prolonged use, nearly all Na^+ gets exchanged.
- Zeolite loses sodium exchange capacity.
- Zeolite becomes exhausted.

Regeneration Steps

① Washing : Zeolite bed is washed with clean water.

② Brine Treatment : Bed is treated with 10% concentrated NaCl solution. (This is called Brine)

⑧ REGENERATION REACTIONS

- Calcium-loaded zeolite
  $CaZ + 2NaCl \longrightarrow Na_2Z + CaCl_2$
- Magnesium-loaded zeolite
  $MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$

☆ Thus,
Exhausted zeolite + NaCl → Regenerated zeolite

- The washings are drained.
- Regenerated zeolite can be reused.

⑨ LIMITATIONS OF ZEOLITE PROCESS

① Turbidity
- Turbid hard water enters zeolite bed.
  → Pores become clogged.
  → Activity decreases.

⇒ Turbidity must be removed before zeolite treatment.

② Iron & Manganese
- Water containing Fe and Mn ions forms FeZ / MnZ.
- These cannot be easily regenerated using brine.

⇒ Fe^{2+} / Mn^{2+} containing water is unsuitable without prior treatment.

③ Acidic Water
- Acidic water can destroy the zeolite bed.

⇒ Acidic water must first be treated with soda, then used in zeolite process.

⑩ ADVANTAGES OF ZEOLITE PROCESS

① Compact Equipment
- Equipment compact, requires less space.
- Does not require highly skilled labour.

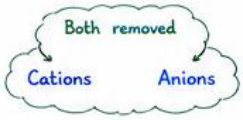
② No Sludge Disposal
- No impurities are precipitated.
- No sludge formation.
- No sludge disposal problem.

③ Installation in Water Supply Line
- Plant can be installed directly in water supply line.
- Double pumping is not required.

④ Very Low Hardness
- Produces water with hardness ≈ 10 ppm
  (Under ideal conditions → 0 ppm)

⑪ ION-EXCHANGE / DEMINERALIZATION PROCESS

Definition: The process of complete removal of all ions present in water is called Demineralization of Water.



⑫ ION-EXCHANGE RESINS

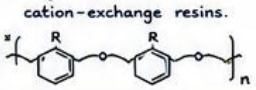
- Ion-exchange resins are cross-linked, long-chain organic polymers.
- They are microporous and insoluble in water.
- Their attached functional groups are responsible for ion exchange.

Two Functional Types

Acidic Functional Groups	Basic Functional Groups
• Can exchange H^+ ions with other cations. (H^+)	• Can exchange their anions with anions present in water. (Cl^-)

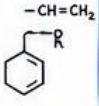
⑬ CATION-EXCHANGE RESINS

- Cation exchange resin is represented as RH^+.
- These resins contain acidic functional groups such as:
  $-COOH$ $-SO_3H$
- They are called cation-exchange resins.



Preparation / Nature

- These resins are mainly styrene-divinylbenzene copolymers.
- After carboxylation or sulphonation, they become capable of exchanging their H^+ ions with cations present in water.



IN ONE LINE
Zeolite softening → Na_2Z exchanges Na^+ for Ca^{2+}/Mg^{2+} → soft water → Zeolite exhausted → 10% NaCl brine → regeneration.

EXAM TIP
Cold Lime-Soda → 50–60 ppm (coagulant needed)
Hot Lime-Soda → 20–30 ppm (no coagulant)

KEY FORMULAS TO REMEMBER
- Zeolite formula : $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$
- Regeneration : $CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$
  $MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$

1 ACIDIC STRENGTH OF CATION-EXCHANGE RESINS

Cation-exchange resins contain acidic functional groups.
Their strength depends on the functional group present.

- **Strongly acidic resin**
  Resins containing $-SO_3H$ groups
  → Strongly acidic resins

- **Weakly acidic resin**
  Resins containing $-COOH$ groups
  → Weakly acidic resins

2 ANION-EXCHANGE RESINS

Definition: Resins containing basic functional groups are called Anion-exchange resins.

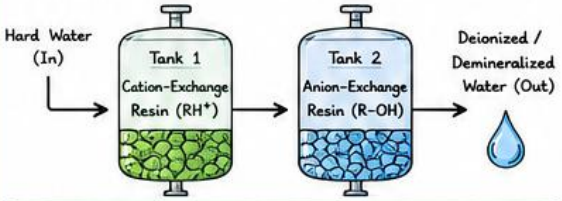
Examples of basic functional groups:

- Amine $-NH_2$
- Substituted amine $-NHR$
- Quaternary ammonium $-NR_4^+$
- Quaternary phosphonium $-PR_4^+$
- Tertiary sulphonium $-SR_3^+$

- These resins are generally styrene-divinylbenzene copolymers.
- They exchange their anions with anions present in water.

3 ION-EXCHANGE PROCESS FOR REMOVAL OF HARDNESS

The ion-exchange unit consists of two tanks arranged in sequence.



Process Flow:

Hard Water → Tank 1 (Cation) → Tank 2 (Anion) → H_2O

(Ca^{2+} / Mg^{2+} removed → H^+ released)
($H^+ + OH^- \rightarrow H_2O$)
(Anions removed → OH^- released)

4 STEP 1 – CATION EXCHANGE

Hard water first enters the cation-exchange tank.
The resin exchanges its H^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water.

- For calcium:

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

- For magnesium:

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

Thus: Ca^{2+} / Mg^{2+} → removed by cation resin
H^+ → released into water

5 STEP 2 – ANION EXCHANGE

After passing through cation-exchange tank, water still contains anions (SO_4^{2-}, Cl^-, CO_3^{2-}, OH^- etc.).
The water is now passed through anion-exchange tank.
The anion resin removes these anions.

- Chloride ion (Cl^-):

$$R-OH^- + Cl^- \longrightarrow R-Cl + OH^-$$

- Sulfate ion (SO_4^{2-}):

$$2R-OH^- + SO_4^{2-} \longrightarrow (R)_2SO_4 + 2OH^-$$

- Carbonate ion (CO_3^{2-}):

$$2R-OH^- + CO_3^{2-} \longrightarrow (R)_2CO_3 + 2OH^-$$

6 FORMATION OF PURE WATER

After passing through both exchangers:

Cation exchanger provides H^+

Anion exchanger provides OH^-

These combine:

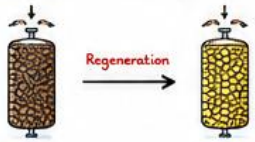
$$H^+ + OH^- \longrightarrow H_2O$$

Therefore, water becomes free from:
✓ Cations ✓ Anions

The resulting water is:
Deionized / Demineralized Water

7 REGENERATION OF ION-EXCHANGE RESINS

- During operation, resins gradually lose their exchange capacity.
- When they can no longer effectively exchange H^+ / OH^-, they are considered EXHAUSTED.
- They must then be regenerated.



8 REGENERATION OF CATION-EXCHANGE RESIN

Step 1 – Backwashing
The resin is first backwashed.

Step 2 – Acid Treatment
A dilute acid solution is passed through the resin.
≈ 2% HCl
or
2% H_2SO_4

Regeneration Reactions:

- Calcium-loaded resin:

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

- Magnesium-loaded resin:

$$R_2Mg^{2+} + 2H^+ \longrightarrow 2RH^+ + Mg^{2+}$$

9 WASHING OF CATION EXCHANGER

After acid regeneration, the column is washed with DEIONIZED WATER.

This removes:
- Ca^{2+}
- Mg^{2+}
- Cl^-
- SO_4^{2-}

The waste washing is drained.
→ Cation exchanger becomes ready for further use.

10 REGENERATION OF ANION-EXCHANGE RESIN

Step 1 – Backwashing
The resin is first backwashed.

Step 2 – NaOH Treatment
A solution of DILUTE NaOH is passed through the resin.

Regeneration Reactions:

- Sulfate-loaded resin:

$$(R)_2SO_4^{2-} + 2OH^- \longrightarrow 2R-OH^- + SO_4^{2-}$$

- Chloride-loaded resin:

$$(R)Cl^- + OH^- \longrightarrow R-OH^- + Cl^-$$

11 FINAL WASHING

After regeneration, the column is washed with DEIONIZED WATER.

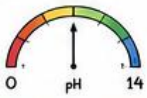
This removes:
- Na^+
- SO_4^{2-}
- Cl^-

The washing is drained.
The regenerated exchanger is
READY FOR FURTHER USE.

12 ADVANTAGES OF ION-EXCHANGE PROCESS

1 Highly Acidic / Alkaline Water Can Be Treated

- Unlike some other softening methods, highly acidic water can be softened.
- Highly alkaline water can also be softened.



2 Very Low Hardness

The process produces water with hardness of approximately

2 ppm

(This is very low hardness water.)

3 Suitable for Boiler Feed

Because both cations and anions are removed:
- Problems such as caustic embrittlement are reduced.
- Corrosion is reduced.

Therefore, the resulting water can be used for BOILER FEED PURPOSE.

13 DISADVANTAGES OF ION-EXCHANGE PROCESS

1 High Cost

- Both equipment and chemicals are expensive.
- Therefore, process is costly.

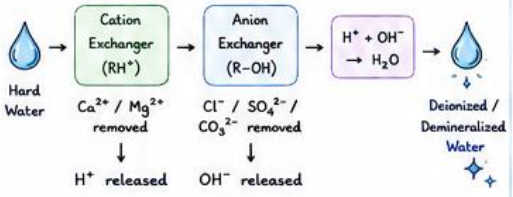
2 Turbid Water Cannot Be Used Directly

- Turbid water reduces efficiency of ion-exchange resins.
- Therefore, turbidity must be removed before ion-exchange treatment.

14 CATION vs ANION EXCHANGE RESINS

Feature	Cation Resin	Anion Resin
Functional Nature	Acidic	Basic
Main Ion Supplied	H^+	OH^-
Removes	Cations	Anions
Examples Removed	Ca^{2+}, Mg^{2+}	Cl^-, SO_4^{2-}, CO_3^{2-}
Regeneration	HCl / H_2SO_4	NaOH
Result in Water	H^+ released	OH^- released

15 COMPLETE DEMINERALIZATION SEQUENCE



16 QUICK SUMMARY (ALL METHODS)

Feature	Lime-Soda	Zeolite	Ion-Exchange
Principle	Precipitation	Cation Exchange	Cation + Anion Exchange
Main Material	$Ca(OH)_2$ + Na_2CO_3	Na_2Z	Ion-Exchange Resins
Sludge	Large amount	No precipitate	No precipitate
Typical Hardness	Higher	~10 ppm	~2 ppm
Regeneration	—	10% NaCl	Acid + NaOH
Cost	Economical	Moderate	Costly
Boiler Suitability	Limited	Better	Suitable

IN ONE LINE

Cation exchanger removes cations → Anion exchanger removes anions → $H^+ + OH^- \rightarrow H_2O$ → Deionized / Demineralized water.

EXAM CHAIN

Hard water → RH^+ resin → Ca^{2+} / Mg^{2+} removed → $R-OH$ resin → anions removed → $H^+ + OH^- \rightarrow H_2O$

EXAM TIP

- Cation resin → acidic → H^+ exchange → regenerate with acid.
- Anion resin → basic → OH^- exchange → regenerate with NaOH.
- Ion-exchange water → ~2 ppm hardness.
- Main disadvantage → costly equipment + chemicals; turbid water reduces resin efficiency.